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U.S. PTO

PATENT APPLICATION TRANSMITTAL LETTER

ATTORNEY'S DOCKET NO.  
BRUNNER ET AL 1

TO THE COMMISSIONER OF PATENTS AND TRADEMARKS:

Transmitted herewith for filing is a patent application of Roland BRUNNER, Helmut Schwenk,  
Johann ZACH

FOR: PROCESS FOR THE WET CHEMICAL TREATMENT OF SEMICONDUCTOR WAFERS  
ENCLOSED ARE:

- sheet(s) of formal drawing(s)  
 sheet(s) of informal drawing(s)  
 an Assignment of the invention, with required cover sheet, to  
WACKER-SILTRONIC GESELLSCHAFT FÜR HALBLEITERMATERIALIEN AG

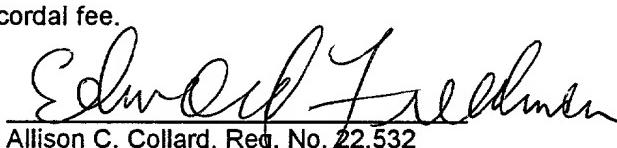
- Priority is claimed under 35 USC 119 for the following application(s):  
GERMANY Patent Appln. No.198 53 486.8NOVEMBER 19, 1998  
 a certified copy of the aforesaid application is enclosed.  
 a certified copy of the aforesaid application will be submitted in due course.  
 Associate Power of Attorney enclosed.

CLAIMS AS FILED

FOR	NUMBER FILED	NUMBER EXTRA	RATE	FEES
TOTAL CLAIMS	10 -- 20	0	X \$18.00	\$ 0.00
INDEPENDENT CLAIMS	1 -- 3	0	X \$78.00	\$ 0.00
BASIC FEE(\$760)				
REDUCED FEE (\$380)	<input type="checkbox"/> Independent Inventor	<input type="checkbox"/> Small Business Concern		\$760.00
			<u>TOTAL FILING FEE:</u>	<u>\$760.00</u>

- Verified Statement of  Independent Inventor  Small Business Concern  
 The Commissioner is hereby authorized to charge any additional fees which may be required at any time during the prosecution of this application without specific authorization, except for the Base Issue Fee, or credit any overpayment to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed.  
 A Check in the amount of \$ 760.00 is enclosed. This check covers:  
 the filing fee  
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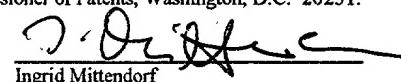
Date OCT. 22, 1999

  
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UNITED STATES SPECIFICATION

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT WE, ROLAND BRUNNER, HELMUT SCHWENK, JOHANN ZACH, all German citizens, reside at Berg 1, D-84367 Reut, Germany; Robert-Koch-Strasse 209, D-84489 Burghausen, Germany; Gambacher Weg 8, D-84347 Pfarrkirchen, Germany, have invented certain new and useful improvements in a

PROCESS FOR THE WET CHEMICAL TREATMENT OF SEMICONDUCTOR WAFERS

of which the following is a specification.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the wet chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, in particular a process for the cleaning of silicon semiconductor wafers.

2. The Prior Art

A treatment process of this type has been described, for example, by *M. Meuris et al. in Solid State Technology, July 1995, p. 109.*

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process by which metallic impurities and particles can be removed particularly effectively from semiconductor wafers.

The above object is achieved according to the present invention by providing a process for the wet chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, wherein the semiconductor wafers are

firstly treated with an aqueous HF solution, then with an aqueous O<sub>3</sub> solution and finally with water or an aqueous HCl solution, these treatments forming a treatment sequence.

It has been found that the object is achieved by this treatment sequence, which does not need to be interrupted by rinsing with water or another treatment liquid and is carried out exclusively at a pH which is lower than pH 7. The treatment according to the invention with the treatment liquids indicated is performed in treatment baths. It is preferable to circulate the treatment liquid, that is to take some of this liquid from the corresponding treatment bath and return it back after having been filtered. This saves on outlay for the required chemicals and for deionized water. The addition of fresh water or other liquids to the treatment baths is to be avoided since, when valves are opened, pressure impulses are created and particles can be introduced into the treatment baths. The treatment according to the invention is therefore different from a rinsing treatment, in which fresh treatment liquid is supplied continuously or at intervals.

The treatments include treating the semiconductor wafers firstly in a bath with an aqueous HF solution, then in a bath with an aqueous O<sub>3</sub> solution and finally in a bath with water or an aqueous HCl solution, form a treatment sequence B<sub>2</sub>. Sequence B<sub>2</sub> may be preceded by a treatment B<sub>1</sub> of the semiconductor wafers in a bath

with an aqueous SC1 solution. An SC1 solution contains NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> or TMAH (= tetramethylammonium hydroxide) and H<sub>2</sub>O<sub>2</sub> is preferred. The treatment sequence B<sub>2</sub> may also be followed by a treatment B<sub>3</sub> of drying the semiconductor wafers. The drying treatment is preferably carried out using the centrifugal, hot water, isopropanol or maran-goni principle.

It is particularly preferable to arrange the sequencing of the treatment of the semiconductor wafers according to the term m\*(B<sub>1</sub> + B<sub>2</sub>) + B<sub>3</sub>, with m being an integer number. The treatment B<sub>1</sub> and the treatment sequence B<sub>2</sub> are carried out in succession, and this takes place m times, before the drying treatment B<sub>3</sub> is performed.

The aqueous HF solution used in the treatment sequence B<sub>2</sub> preferably contains HF in a concentration of from 0.001% to 2% by weight and optionally HCl in a concentration of up to 2% by weight and optionally a surfactant. A mixture of alkylbenzenesulfonate and fatty amine polyglycol ethers in a concentration of 0.001% to 2% by weight is particularly preferred as a surfactant additive. The aqueous O<sub>3</sub> solution used in the treatment sequence B<sub>2</sub> preferably contains O<sub>3</sub> in a concentration of from 1 to 30 ppm and optionally HF in a concentration of from 0.0001% to 2% by weight and is optionally exposed to megasonic waves. The liquid used last in the treatment sequence B<sub>2</sub> is water or an aqueous HCl solution, which preferably contains HCl in a concentration of from 0.001% to 10% by

weight. The liquid may optionally contain O<sub>3</sub> and optionally be exposed to megasonic waves. The temperature of the bath is preferably at a temperature of from room temperature to 80°C.

All percents by weight are based upon the total solution weight.

Other objects and features of the present invention will become apparent from the following detailed description considered in connection with the accompanying examples which disclose embodiments of the present invention. It should be understood, however, that the examples are designed for the purpose of illustration only and not as a definition of the limits of the invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The comparison below of an invention example with comparative examples shows the advantageous effect of the present invention.

The table contains the results (3 sigma values) of conventional counts of particles of specific size (LPD = light point defects), which were in each case carried out on 20 polished semiconductor wafers after a wet chemical treatment sequence and drying which was the same for all the semiconductor wafers.

The example (B) comprised the treatment sequence: HF bath, deionized water/ozone bath, HCl bath with megasonic exposure.

Comparative Example 1 (C1) comprised the treatment sequence: HF bath, deionized water/ozone bath, rinsing with deionized water outside the bath.

Comparative Example 2 (C2) comprised the treatment sequence: HF bath, deionized water/ozone bath with subsequent rinsing using deionized water in the bath and megasonic exposure.

LPD ( $\mu$ M)	>0.3	>0.2	>0.16	>0.12
	Number	Number	Number	Number
B	3	7	30	480
C1	4	13	50	550
C2	10	50	140	550

Accordingly, while a few embodiments of the present invention have been shown and described, it is to be understood that many changes and modifications may be made thereunto without departing from the spirit and scope of the invention as defined in the appended claims.

WHAT IS CLAIMED IS:

1. A process for the wet chemical treatment of semiconductor wafers with treatment liquids, comprising the steps of firstly treating the semiconductor wafers with an aqueous HF solution;

then treating the semiconductor wafers with an aqueous O<sub>3</sub> solution; and

then treating the semiconductor wafers with a liquid selected from the group consisting of water and an aqueous HCl solution;

whereby these treatment steps forming a treatment sequence B<sub>2</sub>.

2. The process as claimed in claim 1,

wherein the treatment sequence B<sub>2</sub> is preceded by a treatment B<sub>1</sub> of the semiconductor wafers with an aqueous SC1 solution.

3. The process as claimed in claim 1,

wherein the treatment sequence B<sub>2</sub> is followed by a treatment B<sub>3</sub> comprising drying the semiconductor wafers.

4. The process as claimed in claim 3,

wherein the treatment of the semiconductor wafers is sequenced according to the term  $m^*(B_1 + B_2) + B_3$ ,  
m being an integer number and the treatment  $B_1$  and the treatment sequence  $B_2$  being carried out in succession, and  
this taking place m times, before the drying treatment  $B_3$  is performed.

5. The process as claimed in claim 1,  
wherein in treatment sequence  $B_2$ , the aqueous HF solution contains HF in a concentration of from 0.001% to 2% by weight and optionally HCl in a concentration of up to 2% by weight and optionally a surfactant; and

wherein all percents by weight are based upon the total solution weight.

6. The process as claimed in claim 1,  
wherein in treatment sequence  $B_2$ , the aqueous  $O_3$  solution contains  $O_3$  in a concentration of from 1 ppm to 30 ppm and is optionally exposed to megasonic waves.

7. The process as claimed in claim 1,  
wherein the treatment liquid used last in the treatment sequence  $B_2$  contains ozone and is optionally exposed to megasonic waves.

8. The process as claimed in claim 3,  
wherein the drying treatment is carried out using a step  
selected from the group consisting of centrifuging, using hot  
water, using isopropanol, and using marangoni principle.

9. The process as claimed in claim 2,  
wherein in treatment B<sub>1</sub> the aqueous SC1 solution contains  
a liquid selected from the group consisting of NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub>, and  
TMAH (= tetramethylammonium hydroxide) and H<sub>2</sub>O<sub>2</sub>.

10. The process as claimed in claim 1, comprising  
carrying out each treatment with a treatment liquid in a  
bath.

ABSTRACT OF THE DISCLOSURE

A process for the wet chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, has the semiconductor wafers firstly treated with an aqueous HF solution, then treated with an aqueous O<sub>3</sub> solution and finally treated with water or an aqueous HCl solution, these treatments forming a treatment sequence.

**Declaration and Power of Attorney for Patent Application**  
**Erklärung für Patentanmeldungen mit Vollmacht**  
**German Language Declaration**

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides statt:

dass mein Wohnsitz, meine Postanschrift, und meine Staatsangehörigkeit den im Nachstehenden nach meinem Namen aufgeführten Angaben entsprechen.

dass ich, nach bestem Wissen, der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent beantragt wird für die Erfindung mit dem Titel:

## PROCESS FOR THE WET CHEMICAL

## TREATMENT OF SEMICONDUCTOR WAFERS

deren Beschreibung  
(Zutreffendes ankreuzen)

hier beigelegt ist.  
 am \_\_\_\_\_ unter der  
Anmeldungsseriennummer \_\_\_\_\_  
eingereicht wurde und am \_\_\_\_\_  
abgeändert wurde (falls tatsächlich abgeändert)

Ich bestätige hiermit, dass ich den Inhalt der obigen Patentanmeldung, einschliesslich der Ansprüche, durchgesehen und verstanden habe, die eventuell durch einen Zusatzantrag wie oben erwähnt abgeändert wurde.

Ich erkenne meine Pflicht zur Offenbarung irgendwelcher Informationen, die für die Prüfung der vorliegenden Anmeldung in Einklang mit Absatz 37, Bundesgesetzbuch, Paragraph 1.56(a) von Wichtigkeit sind, an.

Ich beanspruche hiermit ausländische Prioritätsvorteile gemäß Abschnitt 35 der Zivilprozeßordnung der Vereinigten Staaten, Paragraph 119, aller unten angegebenen Auslandsanmeldungen für ein Patent oder eine Erfindersurkunde, und habe auch alle Auslandsanmeldungen für ein Patent oder eine Erfindersurkunde nachstehend gekennzeichnet, die ein Anmeldedatum haben, das vor dem Anmeldedatum der Anmeldung liegt, für die Priorität beansprucht wird.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

## PROCESS FOR THE WET CHEMICAL

## TREATMENT OF SEMICONDUCTOR WAFERS

the specification of which  
(check one)

is attached hereto.  
 was filed on \_\_\_\_\_ as

**Application Serial No.**

and was amended on

(if applicable)

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

## German Language Declaration

Prior foreign applications  
Vorherige Anmeldungen

198 53 486.8 (Number) (Nummer)	Germany (Country) (Land)	19 November, 1998 (Day/Month/Year Filed) (Tag/Monat/Jahr eingereicht)
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<u>Priority Claimed</u>	
Priorität beansprucht	
X	<input type="checkbox"/>
Yes	No
Ja	Nein

(Number) (Nummer)	(Country) (Land)	(Day/Month/Year Filed) (Tag/Monat/Jahr eingereicht)
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<input type="checkbox"/>	<input type="checkbox"/>
Yes	No
Ja	Nein

(Number) (Nummer)	(Country) (Land)	(Day/Month/Year Filed) (Tag/Monat/Jahr eingereicht)
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<input type="checkbox"/>	<input type="checkbox"/>
Yes	No
Ja	Nein

Ich beanspruche hiermit gemäss Absatz 35 der Zivilprozessordnung der Vereinigten Staaten, Paragraph 120, den Vorzug aller unten aufgeführten Anmeldungen, und falls der Gegenstand aus jedem Anspruch dieser Anmeldung nicht in einer früheren amerikanischen Patentanmeldung laut dem ersten Paragraphen des Absatzes 35 der Zivilprozessordnung der Vereinigten Staaten, Paragrp 112 offenbart ist, erkenne ich gemäss Absatz 37, Bundesgesetzbuch, Paragraph 1.56(a), meine Pflicht zur Offenbarung von Informationen an, die zwischen dem Anmeldedatum der früheren Anmeldung und dem nationalen oder PCT internationalen Anmeldedatum dieser Anmeldung bekannt geworden sind.

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (Anmeldeseriennummer)	(Filing Date) (Anmeldedatum)
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(Status) (patentiert, anhängig, aufgegeben)	(Status) (patented, pending abandoned)
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(Application Serial No.) (Anmeldeseriennummer)	(Filing Date) (Anmeldedatum)
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(Status) (patentiert, anhängig, aufgegeben)	(Status) (patented, pending abandoned)
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Ich erkläre hiermit, dass alle von mir in der vorliegenden Erklärung gemachten Angaben nach meinem besten Wissen und Gewissen der vollen Wahrheit entsprechen, und dass ich diese eidesstattliche Erklärung in Kenntnis dessen abgebe, dass wissentlich und vorsätzlich falsche Angaben gemäss Paragraph 1001, Absatz 18 der Zivilprozessordnung der Vereinigten Staaten von Amerika mit Geldstrafe belegt und/oder Gefängnis bestraft werden koennen, und dass derartig wissentlich und vorsätzlich falsche Angaben die Gültigkeit der vorliegenden Patentanmeldung oder eines darauf erteilten Patentes gefährden können.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## German Language Declaration

**VERTRETUNGSVOLLMACHT:** Als benannter Erfinder beauftrage ich hiermit den nachstehend benannten Patentanwalt (oder die nachstehend benannten Patentanwälte) und/oder Patent-Agenten mit der Verfolgung der vorliegenden Patentanmeldung sowie mit der Abwicklung aller damit verbundenen Geschäfte vor dem Patent-und Warenzeichenamt:

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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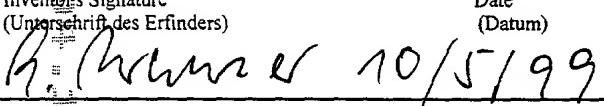
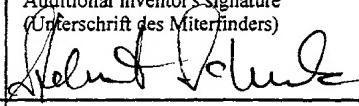
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	10/5/99		10/5/99
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Residence (Wohnsitz)	Residence (Wohnsitz)		
Citizenship (Staatsangehörigkeit)	Citizenship (Staatsangehörigkeit)		
Post Office Address (Postanschrift)	Post Office Address (Postanschrift)		